subset of second-order satellites in the former might invalidate the apparent equivalence of both results.

Summarizing, we conclude that a less-favorable case could hardly be dealt with by the high-symmetry SSG description using the formalism as it stands in, for example, Yamamoto's *REMOS*. On the other hand, none of the above-stated problems appears when the correct structure-factor formula (20)–(21) for the high-symmetry SSG description is employed: no ambiguity appears in the indexing of the diffraction pattern, no reflections must be ignored and no non-symmetry-imposed conditions result for the modulation functions. Thus, the advantages of employing a high-symmetry SSG description will be fully exploited in the resolution of commensurate modulated structures only after the proposed modifications to the structure-factor formula are taken into account.

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A New Algorithm for Computation of X-ray Multiple Bragg Diffraction

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Abstract

A new method for computation of X-ray multiple Bragg diffraction in perfect crystals is presented. The method is based on the extended dynamical diffraction theory and implies the reduction of the diffraction equations to a generalized eigenvalue problem. The advantage of the proposed approach is the possibility of decreasing the scattering-matrix size and simplifying the solution when some X-ray beams are not grazing. The boundary conditions are also simplified by the analysis of Bloch-wave structure inside the crystal and the proper selection of their polarization states.

1. Introduction

In recent years, application of bright synchrotron radiation to a broad range of X-ray experiments has aroused interest in X-ray multiple Bragg diffraction, giving us a new opportunity to measure the fine structure of multiple Bragg peaks. These measurements can form the basis for new methods of studying crystals and their surfaces (see Golovin, Imamov & Kondrashkina, 1985; Kazimirov, Kovalchuk, Kohn, Ishikawa & Kikuta, 1991; Kazimirov, Kovalchuk, Kohn, Kharitonov, Samoilova, Ishikawa, Kikuta & Hirano, 1993; Kohn, 1988; Kohn & Samoilova, 1992; Kov'ev & Simonov, 1986; Stepanov, Kondrash kina & Novikov, 1991; Stepanov, Kondrashkina, Novikov & Imamov, 1994). However, they require a proper theoretical interpretation.

The theoretical analysis of X-ray multiple diffraction in perfect crystals can be based on the dynamical diffraction equations with respect to $2N$ wavefield amplitudes (the factor 2 is due to the vectorial nature of electromagnetic waves). As shown by Kohn (1976, 1979), these equations can be reduced to a simply soluble routine eigenvalue problem for a $2N \times 2N$ scattering matrix.

The problem becomes considerably more complicated if at least one X-ray beam grazes the crystal surface and consequently experiences specular reflection. These grazing cases are of special interest for crystal-surface studies. Also, accounting for specular reflection is often important in the rapidly developing optics of soft X-rays.

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Colella (1974) proposed a method of reducing the diffraction problem for grazing cases to a $4N \times 4N$ scattering-matrix eigenvalue problem. We should note that Colella's work was a great achievement for that time. But we have now gained experience in two-beam grazing-incidence diffraction studies, which enables us to propose essential improvements to Colella's method. In particular:

(1) As follows from diffraction physics in the N-beam diffraction case, there are not $4N$ but only $2(N + N_S)$ strong wavefields inside the crystal, where N_S is the number of grazing X-ray beams. So, Colella's method may supply more solutions than are required. In fact, the unnecessary $2(N - N_S)$ solutions are later left out in his method during the analysis of boundary conditions for X-rays. However, we can obtain a considerable gain in the speed and the simplicity of calculations if we reformulate the eigenvalue problem for the $2(N+N_S) \times 2(N + N_S)$ matrix. For example, in the case of eight-beam X-ray diffraction with only one grazing beam, we could operate with an 18×18 matrix instead of a 32×32 one. A variant of the improved algorithm has been proposed by Stetsko (1990) but his approach is valid for cubic crystals only.

(2) The eigenvalue problem was formulated by Colella for the parameter $k/K \simeq 1$, where k and K are the magnitudes of X-ray wave vectors inside and outside the crystal. It is well known that the deviations of k/K from unity by $\sim 10^{-6}$ have a strong effect on the X-ray diffraction pattern. Therefore, the numerical computations in Colella's algorithm must be carried out with double precision, which is not necessary if we reformulate the problem using $(k/K - 1)$.

(3) Colella's method does not directly account for the change in the exit angles of grazing X-rays as a function of deviations from the Bragg condition. This strong effect is now well known from two-beam grazing-incidence diffraction studies (Afanas'ev & Melkonyan, 1983; Aleksandrov, Afanas'ev & Stepanov, 1984*b*; Baryshevsky, 1976) and should be displayed in multiple diffraction as well.

As a result of the above-listed drawbacks, Colella's method has not been used very often. Researchers have usually confined themselves to studies of particular multiple-diffraction cases where an analytical approach was possible (Hung & Chang, 1989; Stepanov, Kondrashkina & Novikov, 1991; Tseng & Chang, 1990).

In this paper, we propose a new algorithm for the computation of X-ray multiple Bragg diffraction accounting for the grazing beams. Our approach is based on the reduction of the diffraction problem to a generalized eigenvalue problem and is believed to be free from the noted shortcomings.

In § 2, the formulation and solution of the diffraction problem inside a crystal are described. In § 3, we discuss the boundary conditions. § 4 contains several examples of testing computations and some conclusions. In the Appendix, we give formulae necessary for application of the proposed algorithm to experimental data processing.

2. Solution of the diffraction problem inside a crystal plate

As was shown by von Laue (1931), the X-ray wavefield inside the crystal in the case of N-beam dynamical Bragg diffraction can be represented as a superposition of N Bloch waves with wave vectors $\mathbf{k}_h$. Vector amplitudes $\mathbf{D}_h$ of these Bloch waves satisfy the following set of $2N$ linear equations (see, for example, details in the book by Pinsker, 1978):

$$[(k_h^2 - K_0^2)/k_h^2]D_h^s = \sum_{h'} \sum_{s'} \chi_{hh'}(\mathbf{e}_h^s \cdot \mathbf{e}_{h'}^{s'})D_{h'}^{s'}. \quad (1)$$

Here, D_h^s and $\mathbf{e}_h^s$ are the amplitudes and unit vectors of the expansion of vectors $\mathbf{D}_h$ into two mutually normal polarization states: $\mathbf{D}_h = D_h^\sigma \mathbf{e}_h^\sigma + D_h^\pi \mathbf{e}_h^\pi$, $\mathbf{e}_h^\sigma \perp \mathbf{k}_h$, $\mathbf{e}_h^\pi = [\mathbf{e}_h^\sigma \times \mathbf{k}_h]/k_h$. Indexes s, $s' = \sigma$, π denote the polarization states. Indexes h, $h' = 0, \ldots, N-1$ list the reciprocal-lattice vectors $\mathbf{h}$, $\mathbf{h}'$ involved in the diffraction process. The parameters $\chi_{hh'}$ are components of the expansion of the crystal dielectric susceptibility in a Fourier series with respect to $(\mathbf{h} - \mathbf{h}')$. K_h and k_h are the magnitudes of X-ray wave vectors outside the crystal and the respective Bloch-wave vectors inside the crystal. All the K_h have the same value owing to the wavelength preservation in Bragg diffraction: $K_h = K_0 \equiv \omega$. For the Bloch waves, the following condition is known to be satisfied:

$$\mathbf{k}_h = \mathbf{k}_0 + \mathbf{h}. \quad (2)$$

Equation (1) gives the principal opportunity to express all the wave amplitudes in terms of the incident-wave amplitude. Besides, N unknown parameters k_h can be found from $(N - 1)$ equations in the form (2) and the requirement for the determinant of (1) to be equal to zero. The latter provides nonzero solutions for the wavefield amplitudes and leads to a $4N$th-order polynomial equation with respect to k_0.

However, we know that the numerical solution of high-order polynomial equations is unreliable and inexpedient. Therefore, it is desirable to transform the problem to another form. This may be done by expressing deviations of all k_h from ω with the help of one parameter.

Consider the case of a plate-shaped crystal (Fig. 1), usual in X-ray diffraction optics. Let $\mathbf{n}$ be a unit vector along the internal normal to the upper surface of the plate. Then, the following equations can be written, owing to the preservation of the lateral components of wave vectors at the crystal boundary:

$$\mathbf{k}_h = \mathbf{K}_h + \omega\varepsilon_h \mathbf{n}. \quad (3)$$

Here, ε_h are dimensionless parameters, characterizing the refraction of X-rays at the surface. Usually $\varepsilon_h \simeq$

$|\chi_{hh'}| \simeq 10^{-6}$ but for grazing beams the refraction effect increases to $\varepsilon_h \simeq |\chi_{hh'}|^{1/2} \simeq 10^{-3}$.

Using (2) and (3) and the condition $K_h = K_0$, we obtain:

$$\mathbf{K}_h = \mathbf{K}_0 + \mathbf{h} - \omega \Delta\varepsilon_h \mathbf{n}, \tag{4}$$

$$\Delta\varepsilon_h \equiv \varepsilon_h - \varepsilon_0 = -\gamma_h \pm (\gamma_h^2 + \alpha_h)^{1/2}, \tag{5}$$

where

$$\gamma_h = (\mathbf{K}_h \cdot \mathbf{n})/\omega \tag{6}$$

are sines of the angles between the X-ray beams and the surface and

$$\alpha_h = [(\mathbf{K}_0 + \mathbf{h})^2 - K_0^2]/\omega^2 \tag{7}$$

are the deviations of the incident X-ray from the Bragg conditions for various $\mathbf{h}$.

So, we have expressed the deviations of all k_h from ω with the help of one small parameter ε_0: $k_h^2 = \omega^2(1 + 2\gamma_h\varepsilon_h + \varepsilon_h^2)$, where ε_h is related to ε_0 by (5). However, the derived equations contain the values γ_h, which can vary considerably for grazing beams depending on α_h, as is known from two-beam grazing-incidence diffraction studies (Afanas'ev & Melkonyan, 1983; Aleksandrov, Afanas'ev & Stepanov, 1984*b*). To determine these variations, one has to evaluate the scalar products of both sides of (4) with $\mathbf{n}$ and then make use of (5) and (6). As a result, we obtain

$$\gamma_h^2 = (\gamma_0 + \gamma_{\varphi h})^2 - \alpha_h, \tag{8}$$

where $\gamma_{\varphi h} = (\mathbf{h} \cdot \mathbf{n})/\omega = 2\sin\Theta_B^{(h)} \sin\varphi_h$, φ_h is the angle between $\mathbf{h}$ and the surface and $\Theta_B^{(h)}$ is the Bragg angle.

As follows from (8), γ_h can vary considerably only for grazing beams, where $|\gamma_h| \leq |\chi_{hh'}|^{1/2}$, as the variations of α_h in Bragg optics are $|\alpha_h| \simeq |\chi_{hh'}|$.

Let us denote $\gamma_h^{\mathrm{Br}} \equiv \gamma_0^{\mathrm{Br}(h)} + \gamma_{\varphi h}$, where $\gamma_0^{\mathrm{Br}(h)} \equiv \gamma_0\,|_{\alpha_h=0}$.* Then, (8) can be rewritten in the form

$$\gamma_h^2 = (\Delta\gamma_0^{(h)} + \gamma_h^{\mathrm{Br}})^2 - \alpha_h, \tag{9}$$

* The introduced parameter γ_h^{Br} is $\pm\gamma_h\,|_{\alpha_h=0}$.

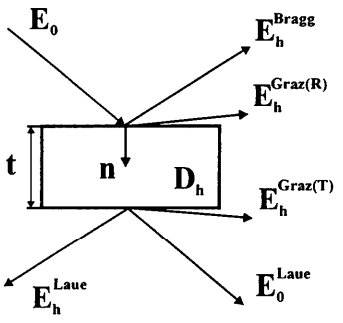

Fig. 1. Schematic presentation of X-ray multiple diffraction in a crystal plate.

where $\Delta\gamma_0^{(h)} = \gamma_0 - \gamma_0^{\mathrm{Br}(h)}$ determines the possible change in the incident angle when the incident beam deviates from the exact Bragg position for $\mathbf{h}$. All $\gamma_0^{\mathrm{Br}(h)}$ may coincide if the incident beam can simultaneously satisfy the Bragg conditions for all reciprocal-lattice vectors involved in the multiple diffraction. Then, we have $\gamma_0^{\mathrm{Br}(h)} \equiv \gamma_0^{\mathrm{Br}}$ and $\Delta\gamma_0^{(h)} \equiv \Delta\gamma_0$. This is always the case for two- and three-beam scattering.

Using (9) and (5), we obtain

$$\Delta\varepsilon_h = -\gamma_h \pm \left|\Delta\gamma_0^{(h)} + \gamma_h^{\mathrm{Br}}\right|. \tag{10}$$

To clarify the sign in (10), one can substitute the right-hand side of (10) into (4) and consider the particular case $\alpha_h = 0$. The sign must be positive if $\gamma_h^{\mathrm{Br}} > 0$ and negative if $\gamma_h^{\mathrm{Br}} < 0$. Therefore, we can write

$$\Delta\varepsilon_h = \Delta\gamma_0^{(h)} + (\gamma_h^{\mathrm{Br}} - \gamma_h). \tag{11}$$

Substitution of (3), (4) and (11) into the left-hand side of (1) yields

$$(k_h^2 - K_0^2)/k_h^2 = \varepsilon_0^2 + 2\varepsilon_0(\gamma_h^{\mathrm{Br}} + \Delta\gamma_0^{(h)}) + \alpha_h. \tag{12}$$

On the basis of (12), the diffraction equations (1) may be written in the form

$$\sum_{h'}\sum_{s'} G_{hh'}^{ss'} D_{h'}^{s'} = \{2(\gamma_h^{\mathrm{Br}} + \Delta\gamma_0^{(h)})\varepsilon_0 + \varepsilon_0^2\} D_h^s, \tag{13}$$

where

$$G_{hh'}^{ss'} = -\alpha_h \delta_{hh'}^{ss'} + \chi_{hh'}(\mathbf{e}_h^s \cdot \mathbf{e}_{h'}^{s'}) \tag{14}$$

is the scattering matrix. As we have already noted, the maximum order of the parameter ε_0 is $\varepsilon_0 \leq |\chi_{hh'}|^{1/2} \simeq \Phi_c$, where $\Phi_c = |\chi_o|^{1/2}$ is known to be the critical angle of X-ray total external reflection. Therefore, the terms with ε_0^2 in the right-hand side of (13) can be neglected for the beams satisfying the condition $|\gamma_h| >> \Phi_c$. As a result, in the absence of grazing beams the diffraction problem is reduced to the generalized eigenvalue problem $G\mathbf{D} = \varepsilon_0(2\Gamma)\mathbf{D}$, where G and 2Γ are square matrices and ε_0 and $\mathbf{D}$ are the eigenvalue and eigenvector of interest. If the equations are divided by $2\gamma_h$, the generalized eigenvalue problem is reduced to the usual one: $G'\mathbf{D} = \varepsilon_0\mathbf{D}$, discussed previously by Kohn (1976, 1979).

In the case of grazing X-ray beams, the solution of (13) becomes more complicated as the terms with ε_0^2 must be taken into account. Nevertheless, these equations can also be linearized by enlarging G and $\mathbf{D}$.

Let the number of grazing beams be N_S ($0 \leq N_S \leq N$), the number of Laue-case beams be N_L and the number of Bragg-case beams be N_B ($N_S + N_L + N_B = N$). Also, let the beams be sorted in decreasing order over γ_h. Then, the first $2N_L$ equations on the right-hand side of (13) contain large $\gamma_h > 0$, corresponding

to Laue-case beams. The subsequent $2N_S$ equations contain small γ_h (grazing beams) and therefore keep ε_0^2 terms. Finally, the last $2N_B$ equations with $\gamma_h < 0$ (Bragg-case beams) are again linear with respect to ε_0. Consequently, (13) can be represented in the following matrix form:

$$G\mathbf{D} = \varepsilon_0(2\Gamma)\mathbf{D} + \varepsilon_0^2\tilde{P}P\mathbf{D}, \tag{15}$$

where $2\Gamma_{hh'}^{ss'} = 2(\gamma_h^{\mathrm{Br}} + \Delta\gamma_0^{(h)})\delta_{hh'}^{ss'}$ is a diagonal matrix, P is the rectangular $2N \times 2N_S$ projection matrix:

$$P = \Big(\underbrace{\boxed{O}}_{2N_L}\ \underbrace{\boxed{I}}_{2N_S}\ \underbrace{\boxed{O}}_{2N_L}\Big)\Big\}2N_S \text{ rows}, \tag{16}$$

I is the unit diagonal matrix, the O are zero rectangular matrices and $\tilde{P}$ is the transposed matrix of P.

Introducing the $2N_S$ component vector $\mathbf{D}_S$:

$$\mathbf{D}_S = \varepsilon_0 P\mathbf{D}, \tag{17}$$

we can rewrite (15) in the linear form

$$G\mathbf{D} = \varepsilon_0[(2\Gamma)\mathbf{D} + \tilde{P}\mathbf{D}_S]. \tag{18}$$

Finally, (17) and (18) can be represented as one matrix equation:

$$\left(\begin{array}{c|c} G & O \\ \hline O & I \end{array}\right)\left(\begin{array}{c} \mathbf{D} \\ \hline \mathbf{D}_S \end{array}\right) = \varepsilon_0\left(\begin{array}{c|c} 2\Gamma & \tilde{P} \\ \hline P & O \end{array}\right)\left(\begin{array}{c} \mathbf{D} \\ \hline \mathbf{D}_S \end{array}\right). \tag{19}$$

Now, the problem of X-ray N-beam dynamical Bragg diffraction is reduced to the generalized eigenvalue problem for this $2(N+N_S) \times 2(N+N_S)$ scattering matrix. The numerical solution of this problem is simply implemented because the respective algorithms are included in the majority of mathematical libraries (see, for example, NAG, 1980). We consider that the computation rate of the new method in some cases can be significantly faster than the one provided by Colella (1974) owing to the smaller matrix size.

The numerical solution of (19) brings $2(N+N_S)$ branches of $\varepsilon_0^{(j)}$ and $(\mathbf{D}^{(j)}, \mathbf{D}_S^{(j)})$.* To determine the contributions of different $\mathbf{D}^{(j)}$ to the total X-ray wavefield, we apply the boundary conditions.

3. Boundary conditions

The X-ray wavefield inside the crystal for every hth X-ray beam can be represented in the form

$$\mathcal{D}_h^s(\mathbf{r}) = \sum_{j=1}^{2(N+N_S)} C_j D_h^{s(j)} \exp(i\mathbf{k}_h^{(j)} \cdot \mathbf{r}), \tag{20}$$

where C_j is the excitation coefficient of the jth solution; $\mathbf{k}_h^{(j)} \equiv \mathbf{k}_h(\varepsilon_0^{(j)})$.

It is shown in (20) that the intensity of each diffracted beam contains the contributions of all solutions. This interference displays the multiple-diffraction interaction. However, it can be proved that there exists a strict connection between the numbers of Laue-case, Bragg-case and grazing-case beams and the types of $\varepsilon_0^{(j)}$. Namely:

(i) every Laue-case beam (including the incident one) provides two solutions (accounting for two polarization states) with slowly decreasing amplitudes along $\mathbf{n}$: $\mathrm{Im}\,\varepsilon_0^{(j)} > 0$;

(ii) every Bragg-case beam provides two roots with slowly increasing amplitudes along $\mathbf{n}$: $\mathrm{Im}\,\varepsilon_0^{(j)} < 0$;

(iii) every grazing beam provides two solutions with strongly increasing and two solutions with strongly decreasing amplitudes.

Kohn (1991) based his arguments on this statement for multiple diffraction without grazing beams. Aleksandrov, Afanas'ev & Stepanov (1984*a*) proved this mathematically for two-wave grazing-incidence diffraction. The simplest argument is that the solutions describe Bloch waves and there should exist a Bloch wave propagating along every beam outside the crystal.

So, in total, we have:

(*A*) $2N_S$ roots with large $\mathrm{Im}\,\varepsilon_0^{(j)} > 0$,

(*B*) $2N_L$ roots with small $\mathrm{Im}\,\varepsilon_0^{(j)} > 0$,

(*C*) $2N_B$ roots with small $\mathrm{Im}\,\varepsilon_0^{(j)} < 0$,

(*D*) $2N_S$ roots with large $\mathrm{Im}\,\varepsilon_0^{(j)} < 0$.

For convenience, we suppose the roots are sorted in the sequence above. Consider a crystal of practical thickness (*e.g.* $t \geq 10\,\mu$m), so that the roots of classes (*A*) and (*D*) satisfy the condition $\left|\mathrm{Im}\,\varepsilon_0^{(j)}\right|\omega t >> 1$. In this case, the last $2N_S$ roots with large $\mathrm{Im}\,\varepsilon_0^{(j)} < 0$ can be excluded from consideration because the respective Bloch waves display large amplitudes at the lower boundary of the plate that are not physically real.* So, the respective $2N_S$ excitation coefficients C_j are assumed equal to zero.

As the solutions of class (*D*) are not excited, we have to put only $2N_S + 2N_S + 2N_S + 2N_L + 2N_B = 2N$ boundary conditions for the determination of the other $2N$ coefficients $C^{(j)}$. Let us consider these conditions separately for three types of beams.

3.1. *Laue-case beams*

The intensity of Laue-case beams at the upper (entrance) surface of the crystal plate is equal to unity for

* The components $\mathbf{D}_S^{(j)}$ are not of physical interest and can be immediately excluded from consideration.

* However, this does not imply that the grazing beams are not able to leave the plate through the lower boundary because their total wavefield determined by (20) contains the contributions of the other solutions. See also the works by Kishino (1971), Kishino, Noda & Kohra (1972) and Hartwig (1976) concerning this problem.

the incident beam and to zero for other beams. Therefore, the following $2N_L$ equations can be written:

$$\mathcal{D}_h^s(0) = \sum_{j=1}^{2N} C_j D_h^{s(j)} = \delta_{h0} \cos \Delta\varphi_s, \qquad (21)$$

where $\Delta\varphi_s$ are the angular deviations of the incident-wave polarization plane from $\mathbf{e}_0^s$.

3.2. *Bragg-case beams*

Similarly, the intensity of Bragg-case waves at the lower boundary of the plate is also equal to zero (another $2N_B$ equations):*

$$\mathcal{D}_h^s(t) = \sum_{j=1}^{2N} C_j D_h^{s(j)} \exp(i\omega\varepsilon_0^{(j)} t) = 0. \qquad (22)$$

3.3. *Grazing beams*

The boundary conditions for grazing beams are set at both upper and lower surfaces. The conditions at the upper surface consist of $2N_S$ equations for X-ray electric fields and $2N_S$ equations for their derivatives. The latter conditions appear because of accounting for refraction. Now, there are $4N_S$ conditions, but they contain $2N_S$ unknown amplitudes $E_h^{s(R)}$ of vacuum grazing beams above the surface. Excluding $E_h^{s(R)}$, one can arrive at $2N_S$ equations derived by Colella (1974). Please note that these equations are considerably simplified if vectors $\mathbf{e}_h^g$ of the grazing waves are chosen parallel to the crystal surface (see, for example, Aleksandrov, Afanas'ev & Stepanov, 1984*b*). In this case, we have

$$\sum_{j=1}^{2N} C_j D_h^{s(j)} (\delta_{h0} + \varepsilon_h^{(j)}/2\gamma_0) = \delta_{h0} \cos \Delta\varphi_s. \qquad (23)$$

The number of conditions at the lower boundary is also equal to $4N_S$ but the conditions for the wavefields and their derivatives coincide because the wavefields do not include class (*A*) ('grazing') solutions at the lower boundary owing to their strong damping. As a result, we have only $2N_S$ equations, which determine $2N_S$ amplitudes $E_h^{s(T)}$ of vacuum grazing beams below the boundary and do not provide the additional conditions for C_j.

Thus, the total set of boundary conditions consists of $2N$ equations. They can be presented in the form of one matrix equation:

$$\sum_{j=1}^{2N} C_j F_h^{s(j)} = \delta_{h0} \cos \Delta\varphi_s, \qquad (24)$$

where the matrix $F_h^{s(j)}$ is given by

$$F_h^{s(j)} = \begin{cases} D_h^{s(j)} & \text{for Laue-case beams,} \\ D_h^{s(j)} \exp(i\omega\varepsilon_0^{(j)} t) & \text{for Bragg-case beams,} \\ D_h^{s(j)} (\delta_{h0} + \varepsilon_h^{(j)}/2\gamma_0) & \text{for grazing beams.} \end{cases} \qquad (25)$$

Equations (25) can be solved numerically by the Gaussian method.*

If the C_j are found, the reflection coefficients of vacuum X-ray waves are evaluated according to the formulae

$$P_h = (|\mathrm{Re}\,\gamma_h|/\gamma_0) \sum_s |\mathcal{D}_h^s(z) - \delta_{h0}\delta_{z0} \cos \Delta\varphi_s|^2, \qquad (26)$$

where $z = 0$ for the beams leaving the crystal through the upper (entrance) surface and $z = t$ for the transmitted beams. Equation (26) is applied to Bragg-case beams at the upper surface, to Laue-case beams at the lower surface and to grazing beams at both surfaces.

4. Numerical examples and discussion

The proposed method has been implemented in a program computing three- to eight-beam X-ray diffraction and some test computations have been carried out.

In the absence of grazing beams, the results of the program coincide completely with those of Kohn (1976, 1979). Therefore, let us consider the grazing cases, where testing is more complicated.

Results from computations for three-beam X-ray reflection 000, 220, 202 from a germanium crystal plate with $(\bar{1}11)$ surface orientation are shown in Fig. 2. The selected wavelength, $\lambda = 3.463683$ Å, provides coplanar diffraction geometry where all the beams graze along the crystal surface. That is the case considered by Hung & Chang (1989) within an analytical formalism.

In Fig. 2(*a*), the computations are carried out for $\alpha_{220} = \alpha_{202} = 100|\chi_0|$. In this case, the rocking curve for beam 000 displays the shape of the X-ray specular reflection curve from amorphous material. This is reasonable because the reflections 220 and 202 are not excited significantly owing to the large α. The reflection coefficients for 220 and 202 are equal to zero because neither of these beams can leave the crystal owing to the total internal reflection effect [as follows from (8), parameters γ_{220} and γ_{202} are imaginary numbers].

Fig. 2(*b*) presents the computations for $\alpha_{220} = 0$ and $\alpha_{202} = 100|\chi_0|$, *i.e.* practically for two-beam diffraction. Respectively, the curves 000 and 220 in the figure

* We can exclude a part of the 'Bragg-case' solutions satisfying the condition: $\mathrm{Im}\,\varepsilon_0^{(j)}\omega t << -1$, if the crystal is sufficiently thick. Simultaneously, the boundary conditions for the respective number of Bragg-case beams with the smallest (*i.e.* the closest to grazing) γ_h are also excluded. This is the same procedure as for class (*D*) ('grazing') roots.

* The boundary conditions for a very thin crystal are formulated identically but with account taken of the refraction of the grazing waves at the lower boundary. As a result, $2(N+N_S)$ conditions for $2(N+N_S)$ values $\varepsilon_0^{(j)}$ are obtained.

coincide with the calculations based on two-beam theory by Afanas'ev & Melkonyan (1983) and Baryshevsky (1976). In particular, the angular dependence for 000 displays the two-threshold specular reflection effect noted by Baryshevsky (1976).

Finally, the computations in Fig. 2(*c*) are carried out for the case $\alpha_{220} = \alpha_{202} = 0$, when both 220 and 202 are excited simultaneously. We see that the two-threshold effect of the specular reflection is enhanced by three-beam diffraction. At the same time, the intensity maxima for 220 and 202 are decreased because these reflections 'share' the incident intensity.

The computations presented correlate in general with the data of Hung & Chang (1989). Some deviations are due to the accounting for absorption in our data being different from that of Hung & Chang (1989).

Concluding, we can state that the method has been implemented and tested. We believe that it can be successfully used in applications of X-ray multiple diffraction to crystal-surface studies and in multibeam optics of soft X-rays. Additionally, it is applicable to studies of reflection high-energy electron diffraction.

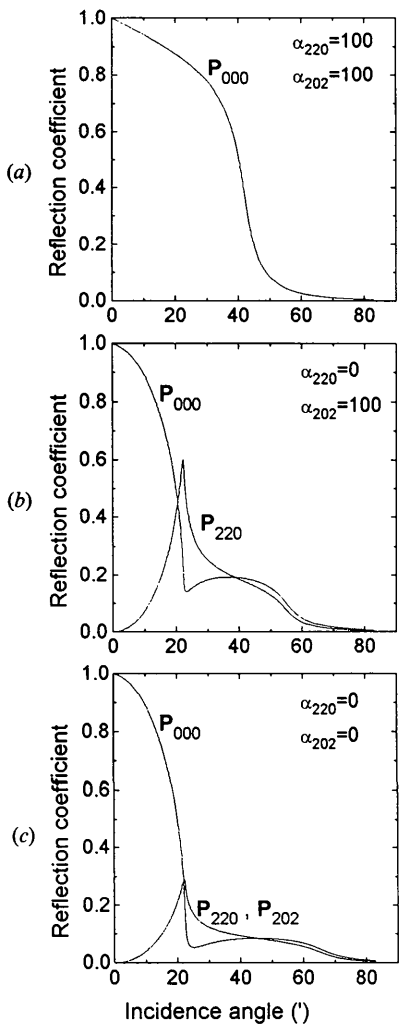

Fig. 2. Rocking curves of three-beam grazing-incidence diffraction 000, 220, 202 in germanium.

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APPENDIX

Here, we give some equations that are useful for the application of this algorithm to experimental data processing.

We present the incident wave vector in the following form:

$$\mathbf{K}_0 = \mathbf{K}_0^{\mathrm{Br}}\{1 - [(\theta_1^2 + \theta_2^2)/2]\} + \omega(\mathbf{a}_1\theta_1 + \mathbf{a}_2\theta_2). \quad (27)$$

Here, $\mathbf{K}_0^{\mathrm{Br}}$ is the wave vector satisfying exact Bragg conditions for $\mathbf{h}_1$ and $\mathbf{h}_2$; θ_1 and θ_2 are the angular deviations of $\mathbf{K}_0$ from $\mathbf{K}_0^{\mathrm{Br}}$; $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors specifying the directions of variations of these angles in the experiment $\{\mathbf{a}_1 \perp \mathbf{k}_0, \mathbf{a}_2 = (\mathbf{a}_1 \times \mathbf{k}_0)/\omega\}$.

Substituting (27) into (7) and (8), we obtain

$$\alpha_h = \alpha_h^{\mathrm{Br}} + [2(\mathbf{a}_1 \cdot \mathbf{h})/\omega]\theta_1 + [2(\mathbf{a}_2 \cdot \mathbf{h})/\omega]\theta_2 + 2\sin^2\Theta_B^{(h)}(\theta_1^2 + \theta_2^2), \quad (28)$$

$$\gamma_0 = \gamma_0^{\mathrm{Br}} + (\mathbf{a}_1 \cdot \mathbf{n})\theta_1 + (\mathbf{a}_2 \cdot \mathbf{n})\theta_2, \quad (29)$$

where $\alpha_{h_1}^{\mathrm{Br}} = 0, \alpha_{h_2}^{\mathrm{Br}} = 0, \alpha_{h_n}^{\mathrm{Br}} = [(\mathbf{K}_0^{\mathrm{Br}} + \mathbf{h}_n)^2 - K_0^2]/\omega^2$, $n > 2$.

Equations (27) and (28) are applicable to the simulation of multiple-diffraction experiments irrespective of the presence or absence of grazing beams.

Note that the quadratic terms in θ are included in (27) in view of possible large-scale variations of these angles. To illustrate this, let us consider the example analyzed in § 3 and choose the direction of θ_1 variations to be along the surface ($\mathbf{a}_1 = [\mathbf{n} \times \mathbf{k}_0]/\omega$). Then, θ_2 is varied parallel to the surface and one can easily find

$$\alpha_h = 2\sin^2\Theta_B^{(h)}\theta_2^2, \qquad \gamma_0 = \gamma_0^{\mathrm{Br}} + \theta_2. \quad (30)$$

These equations show that the variations of the incidence angle cause the changes in all α_h due to θ_2^2 terms. Therefore, a straightforward measurement of the curves presented in Fig. 2 is not possible. This fact has been noted by Stepanov (1991).

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Integration of Patterson Information into Direct Methods. IV. The Use of Interatomic Triangles

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Abstract

A probabilistic approach is described that is able to estimate triplet phase invariants when prior information on interatomic vectors and interatomic triangles is available. The conclusive formula is compared with the vector-interaction formula derived by Hauptman & Karle [*Acta Cryst.* (1962), **15**, 547–550] and with a probabilistic formula obtained *via* maximum-entropy methods.

Symbols and abbreviations

The papers by Giacovazzo (1991) and Altomare, Cascarano & Giacovazzo (1992*a*,*b*) are referred to as papers I, II and III, respectively. Symbols and abbreviations are the same as those used in these papers.

Introduction

In paper I of this series, the standard method of joint probability distribution functions was modified in order to exploit the information provided by a Patterson map. If interatomic vectors $\mathbf{u}_{j_1 j_2} = \mathbf{r}_{j_1} - \mathbf{r}_{j_2}$ are known *a priori*, the symmetry-independent atomic positional vectors cannot be considered as random variables uniformly distributed in the asymmetric unit (indeed, $\mathbf{r}_{j_1}$ is completely determined in terms of $\mathbf{r}_{j_2}$ and $\mathbf{u}_{j_1 j_2}$). The theory provided triplet invariant estimates different from those provided by standard methods. The formula requires prior information both on the coordinates of the peaks and on the scattering factors of the atoms with mutual distance $\mathbf{u}$. Since this second type of information is usually unavailable (for example because of peak overlapping), in paper II the formula was modified to depend on $\mathbf{u}$ and on the corresponding Patterson peak intensity. Some applications were also described.

In paper III, the theory was extended to introduce the information contained in Harker sections.

The main aim of this paper is to describe a probabilistic approach for triplet invariant estimation that is able to exploit the information contained in the interatomic triangles. This type of information includes prior knowledge of interatomic vectors and also takes into account correlation among different interatomic vectors. The problem is correlated with the double Patterson function (Sayre, 1953; Kroon & Krabbendam, 1970) and a first answer was found in an algebraic expression derived by Hauptman & Karle (1962) for the calculation of triplet phases

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